

PROGRESS REPORT NO. 1

FOR

STUDY OF INELASTIC ELECTRON-MOLECULE COLLISIONS

(21 March 1966 - 30 June 1966)

Contract No.: NAS5-9303

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Prepared by

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ABSTRACT

Progress Report No. 1, under Contract NAS5-9303, summarizes the theory being applied to the calculation of the rate of dissociative recombination of N_2^+ and which will be applied in ensuing periods to the ion O_2^+ . Partial results pertaining to N_2^+ are included. No new technology is reported but a study directed toward improvement of existing methods of calculating electronic transitions to continuum states of the nuclear motion is discussed.

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I. INTRODUCTION

The reaction of dissociative recombination is represented as



where A' and B'' represent possibly excited states of the constituent atoms. The fast rates for this reaction, typically 10^{-8} - 10^{-6} cm^3/sec at room temperature, make it dominate electron removal processes in a wide variety of conditions of ionized gases. It is of particular importance in ionized air where NO^+ , N_2^+ , and O_2^+ will be the predominant ions at moderate to high pressures. The objective of the present contract is to extend a previous theoretical calculation of rate of dissociative recombination of NO^+ to the molecular ions N_2^+ and O_2^+ . Such calculations should be useful in studying the chemical kinetics of the ionosphere and of air perturbed by re-entry vehicles or explosions.

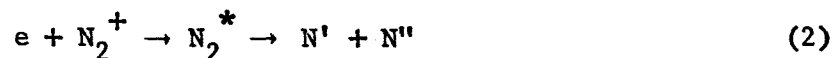
Work began under this contract on 1 April 1966. This report briefly summarizes the work performed over the first of three quarterly periods of this contract, during which approximately 9 man-weeks of study were expended.

The technical discussion is contained in Section II below, and covers a resume of the theory being applied to the N_2^+ reaction and some initial findings. Also included is a discussion of possible improvements in the Winans-Stueckelberg approximation, a widely used method for calculating continuum vibrational wave functions for diatomic molecules. Sections III, IV, and V deal, respectively, with new technology (none yet reported), the program for the next period, and the conclusions arising from the first period study.

II. DISCUSSION

A. SUMMARY OF THEORY OF DISSOCIATIVE RECOMBINATION

Due to the difference in time-scales between the nuclear and electronic motions, the reaction of dissociative recombination is readily approximated by a two-stage reaction



i.e., unimolecular capture of the incident electron into an excited unstable state of N_2 . The critical reaction will occur by means of excitation of a bound electron with a concurrent destruction of the molecular band. The resulting dissociation is in general fast compared to the rate of auto-ionization of the N_2^* state. In this case we have for the cross section

$$v \sigma_{DR} \approx \frac{2\pi 2\hbar^3}{m^2 v} \frac{g_f}{g_i} \frac{\delta(\sum E_i - \sum E_f)}{\tau_{ai}} \quad (3)$$

where g_f and g_i are the statistical weights of the initial and final states, v the incident electron velocity, and τ_{ai} the lifetime for auto-ionization. The delta function yields overall energy conservation and is removed by integrating over a continuum of incident electron energies. Thus

$$\frac{\delta(\sum E)}{\tau_{ai}} \rightarrow \frac{m^2 v}{\pi \hbar^4} \left| \langle v \rangle_{e1} \right|^2 \int \left| \psi_0(R) \right|^2 e^{-E_r(R)/kT_e} dR \quad (4)$$

where $\langle v \rangle_{e1}$, the matrix element of the perturbing potential integrated over the electronic coordinates has been assumed to be approximately

independent of the nuclear coordinates in the transition region. Equations (3) and (4) yield the rate coefficient $\alpha_{DR}(T_e)$ upon substitution into $\alpha_{DR} = \langle v \sigma_{DR} \rangle$, or

$$\alpha_{DR}(T_e) = \left(\frac{2}{kT_e}\right)^{3/2} \left(\frac{\pi}{m}\right)^{1/2} \frac{mv}{\hbar^2} \left| \langle v \rangle_{e1} \right|^2 \int |\psi_0(R)|^2 e^{-E_R/kT_e} dR \quad (5)$$

In order to calculate α we must determine the vibrational wave function $\psi_0(R)$, the energy E_R (which is derivable from the final state potential curve), and the wave functions for the active electrons (which enter into $\langle v \rangle_{e1}$).

The nuclear wave function $\psi_0(R)$ can be accurately determined from the known properties of N_2^+ . Using the studies of F. Gilmore (RAND Corporation Report, RM-4034-PR, June 1964), we have for the ground state $N_2^+ X^2 \Sigma_g^+$,

$$\begin{aligned} \mu_A &= 7.0036 \text{ physical mass units} \\ r_e(N_2^+) &= 1.116 \times 10^{-8} \text{ cm} \\ \omega_e &= 2207.2 \text{ cm}^{-1} \end{aligned} \quad (6)$$

These parameters are sufficient to determine the wave function for the vibrational states of N_2^+ , assuming this motion to be simple harmonic, which it is to a high degree of accuracy for the lower states. The rotational quantum numbers will not be changed in the interaction due to the smallness of the coupling between the electronic perturbation and angular momentum of the ionized molecule. Thus the rotational wave functions "cancel out" in lowest order. The vibrational wave functions are

$$\psi_v(N_2^+) = N_v e^{-1/2\alpha x^2} H_v(\alpha^{1/2}x) \quad (7)$$

where $N_v = (2^v v!)^{1/2} (\alpha/\pi)^{1/4}$, $H_v(Z)$ is a Hermite polynomial, $\alpha = 2\pi\mu_A \omega_e \epsilon/h$, $x = r-r_e$, and where in turn r_e , μ_A , and ω_e are given by Equation (6).

Determination of the parameters for the unstable state N_2^* is much more difficult. The electronic structure of N_2^+ is $KK (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^4 \sigma_g 2p$. In order to destroy the molecular bond one of the bonding orbitals must be excited to an anti-bonding orbital by the incident electron, which itself, must go into an anti-bonding orbital. This will leave a difference between bonding and anti-bonding orbitals in the N_2^* state of 1 as compared to 2-1/2 in the N_2^+ ground state. Thus the intermediate state will have only about 2eV of binding energy. Dissociation will be prompt due to the excess of kinetic energy which will be picked up by the nucleus in the transition.

The most probable final state of the separated N atoms appears to be $N(^2D^0) + N(^2D_0)$ on the basis of a favorable crossing of potential curves (Gilmore, loc. cit.). Since the perturbation is e^2/r_{12} where r_{12} is the distance between the active electrons, the most probable state of N_2^* is a triplet (states of higher multiplicity cannot be reached without spin flip as the N_2^+ state is a doublet). In lowest order perturbation theory neither the sign nor the parity will change so that we are led to the probable final state of N_2^* as a $^3\Delta_g$. For the transition of the active electrons we have

$$(\sigma_g 2p) (K2p) \rightarrow (\sigma_u 2p)^2 \quad (8)$$

where $(K2p)$ represents the 2p component of the incident Coulouf wave with momentum K.

Numerical calculations involving a Morse potential are underway for the calculation of the nuclear matrix elements according to Equations (5), (6), and (7) above. The electronic wave functions are being approximated by Slater orbitals with an effective charge Z' to account for screening.

B. CONCERNING THE WINANS-STUECKELBERG APPROXIMATION FOR CONTINUUM WAVE FUNCTIONS

The above theory uses the well-known Winans-Stueckelberg approximation (Proc. National Academy of Sciences, U.S.A., Vol. 14, 867, 1928) for the vibrational wave functions. This approximation is based on the Franck-Condon principle which holds that, to a first approximation, neither the position nor velocity of the nuclear motion changes in an electronic transition. Thus the continuum wave function is found by a reflection of the initial state function in the potential curve for the continuum state. That is, $\psi_f(E) \rightarrow \psi_o(R(E))$ where $R(E)$ is the inverse function to $E(R)$, the difference between the initial energy of bound state and the potential energy of the final state. This semi-classical description should be reasonably accurate for higher vibrational states where the nuclear motion can be localized. For lower levels, however, it is possible that an improvement can be made to account for the finite size of the nuclear wave packet in the final state. This should yield a small numerical correction to our theory of dissociative recombination. Initially, WKB wave functions are being investigated for the final continuum state.

III. NEW TECHNOLOGY CLAUSE

It is not believed that there were any innovations or inventions during this period which are reportable under this clause.

IV. PROGRAM FOR THE NEXT PERIOD

Completion of the numerical integration of the nuclear and electronic matrix elements for the N_2^+ molecule is planned. Initial study of the O_2^+ dissociative recombination should commence near the end of this period.

V. CONCLUSIONS AND RECOMMENDATIONS

Partial technical results which have been obtained during this period are given above in Section II. It is recommended that work on this program continue in order to increase our understanding of recombination processes, especially at elevated temperatures in atmospheric gases. Based on the results obtained so far no re-direction of the work effort is advised.